Polymer Gels

Boulder Lectures in Soft Matter Physics
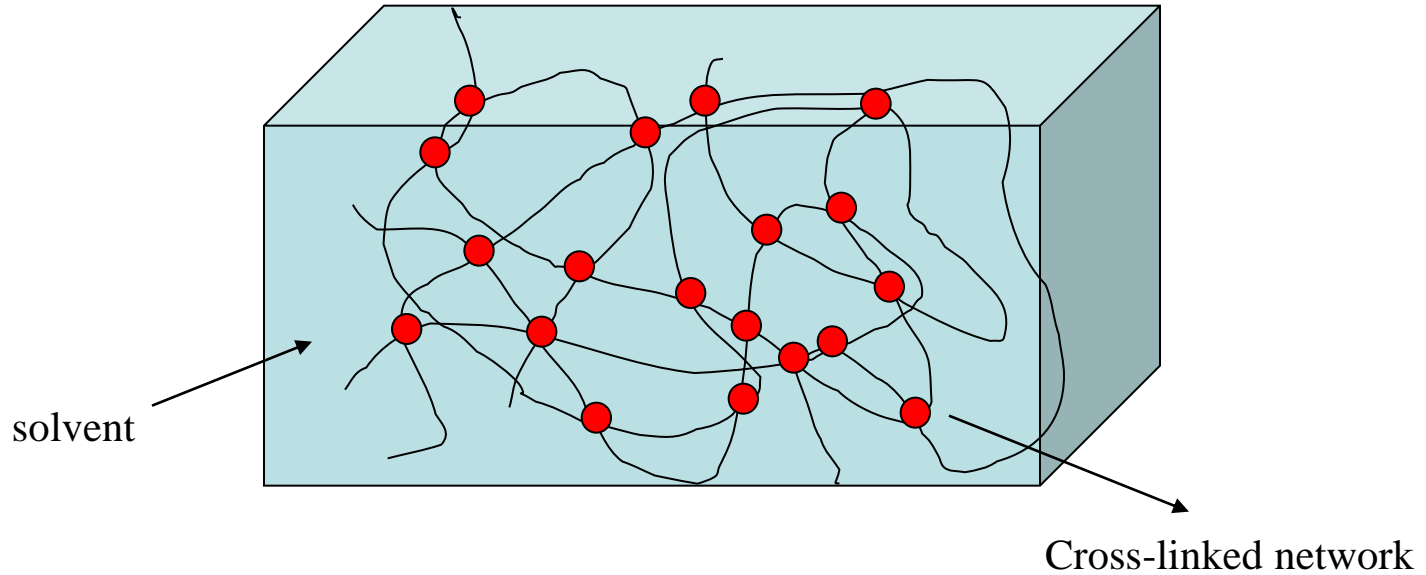July 2012
Yitzhak Rabin

- M. Rubinstein and R.H. Colby, "*Polymer Physics*" (Oxford, 2003), Chapters 6 and 7
- P.-G. de Gennes, "*Scaling Concepts in Polymer Physics*" (Cornell, 1979), Chapter 5
- S. V. Panyukov and Y. Rabin, "Statistical Physics of Polymer Gels", Phys. Rep. **269**, 1 (1996)

Gel – polymer network permeated by solvent

solvent

Cross-linked network

polymer volume fraction ≈ 0.1-10 %

Gelation

physical bonds   chemical (covalent bonds)

Weak   Strong   Reacting monomers   Crosslinking polymers
(Vulcanization)

Condensation
(Critical Percolation)
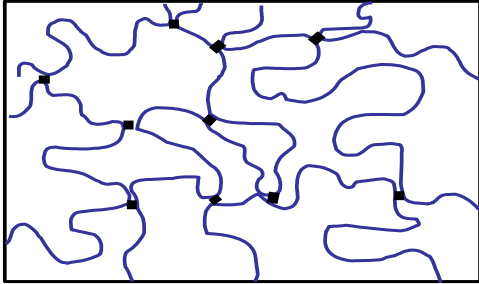
Addition
(Kinetic Growth)

End-linking

Random
Crosslinking

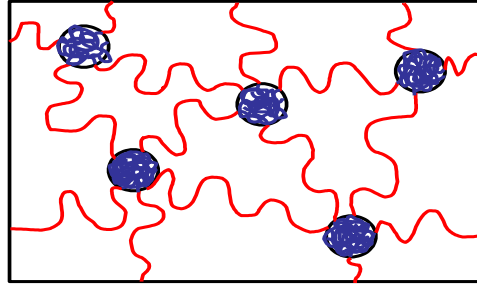Chemical and strong physical gels are soft solids
– macroscopic elasticity

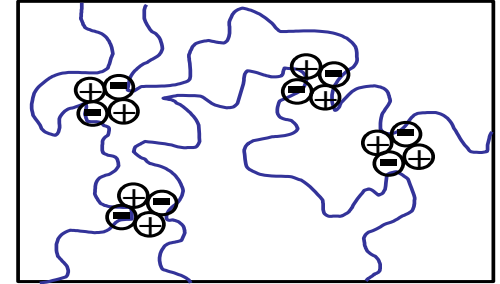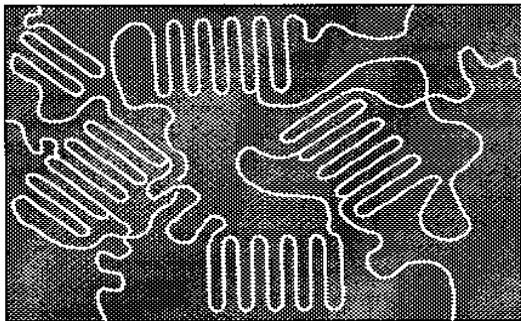Weak physical gels are viscoelastic liquids

Physical bonds

Hydrogen bonds

Block copolymer nodules
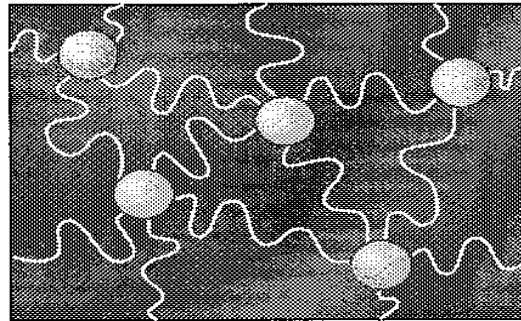
Ionic associations

Microcrystal lamellae

Glassy nodules
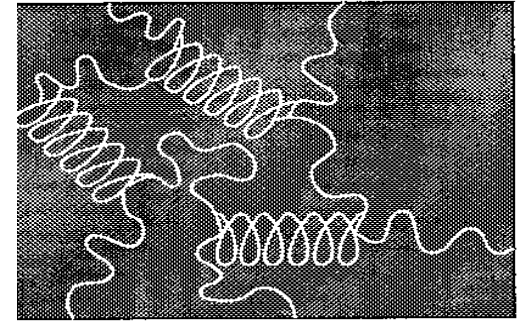
Double helices

Here we focus on "solid" (strong) gels:
- irreversible crosslinking
- stable in solvent bath but solvent evaporates when exposed to air

Evaporation is diffusion-controlled:
10^{-6} cm^2/s $\longrightarrow$ t 1 week, for a 1cm^3 gel

Gelation is a random process –
no two gels have identical structure (topology) even if identically prepared!

$\downarrow$

Unique speckle patterns in light scattering

Are gels equilibrium solids or glasses?

(single vs multiple equilibrium states)

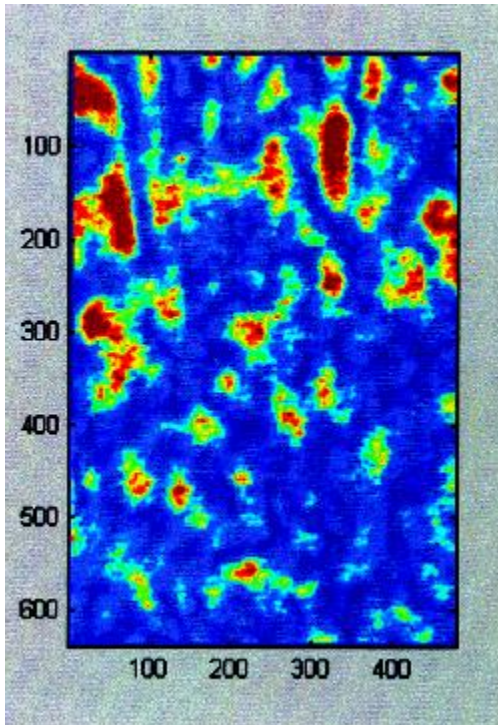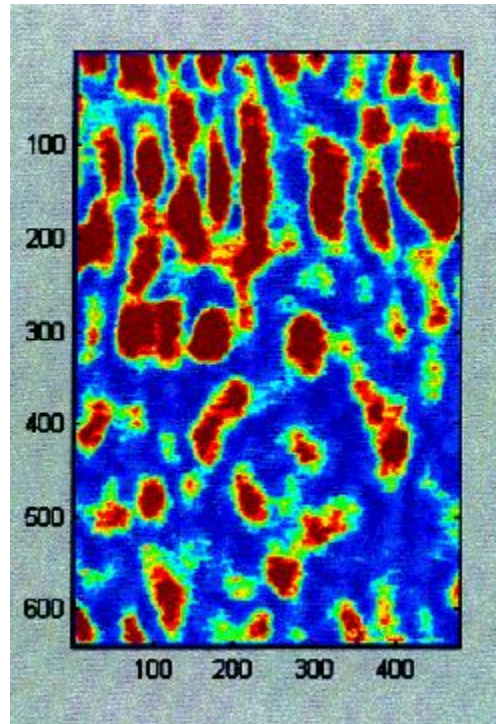Determine uniqueness of $\rho^{eq}(r)$ by temperature cycling $\quad T_1 \to T_2 \to T_1$

and monitoring the speckle patterns

$35^{\circ}C$ $\qquad\qquad\qquad$ $45^{\circ}C$ $\qquad\qquad\qquad$ $35^{\circ}C$

Goren et al, *Macromolecules* **33**, 5757 (2000).
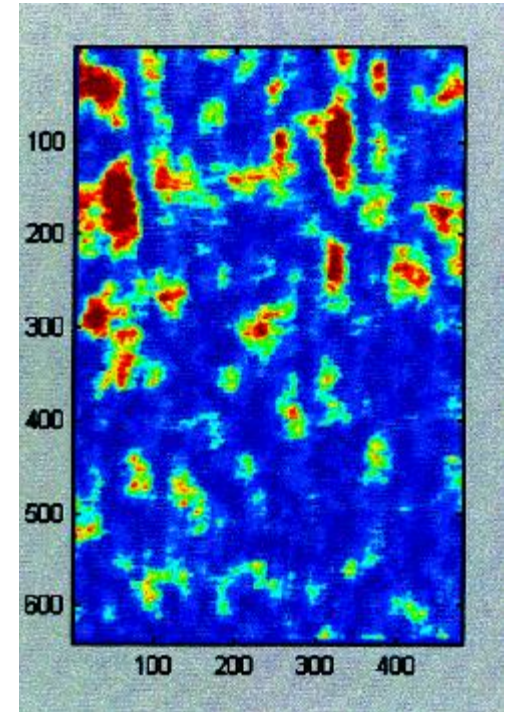
Gelation:

Dilute solution of monomers M ($f=2$) with volume fraction ϕ_M and crosslinks C ($f>2$) with volume fraction ϕ_C

$$\phi_C < \phi_M < 1$$

If $\phi_C \ll \phi_M$ only small connected clusters ("sol") exist

An infinite cluster ("gel") appears at ϕ_C^* - Gel point

Shear rigidity first appears at $\phi_C^{**} > \phi_C^*$

- much of theory focuses on the sol-gel transition because of the connection to percolation and critical phenomena

Bond percolation: bonds introduced with probability p
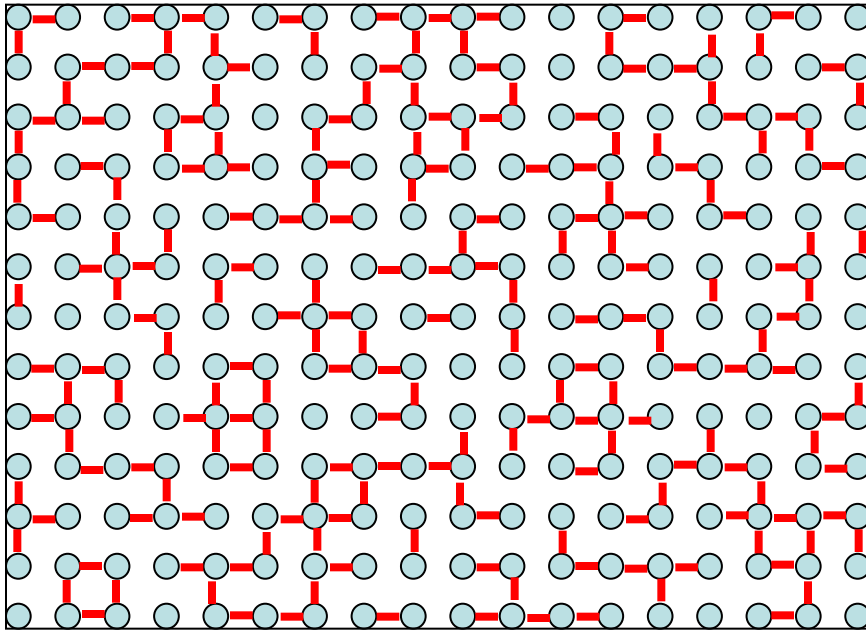
$p < p_c$
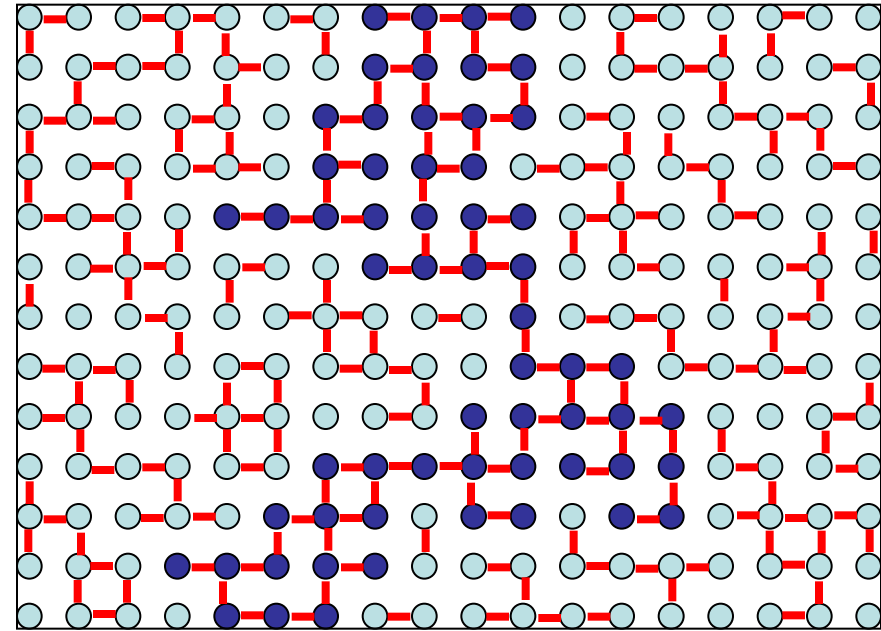
$p > p_c$

Extent of reaction p – fraction of formed bonds out of all possible bonds.

Connectivity transition at critical extent of reaction p_c (percolation threshold).

Only finite clusters (sol) at $p<p_c$.

At $p>p_c$ – "infinite" cluster (gel), in addition to finite clusters.

Mean-field estimate of the gel point
(neglect loops)

Condensation polymerization of AB_{f-1} monomers:
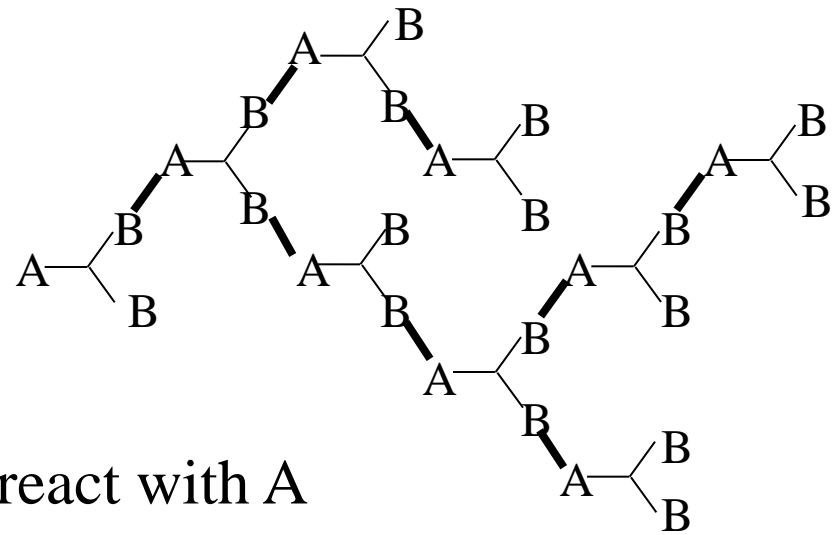
p – probability of B to react with A

Fraction of reacted A groups: *p(f-1)*

Maximum extent of reaction (all A groups reacted): $p_c=1/(f-1)$

Each branched polymer contains only one unreacted A group –
molecules = # unreacted A groups

$$\text{———} = 1 - p(f-1) = \text{——}$$

Average polymer size: ——— = —— diverges at !

Elasticity of networks

$$\vec{R} = \lambda \, \vec{R}_0$$
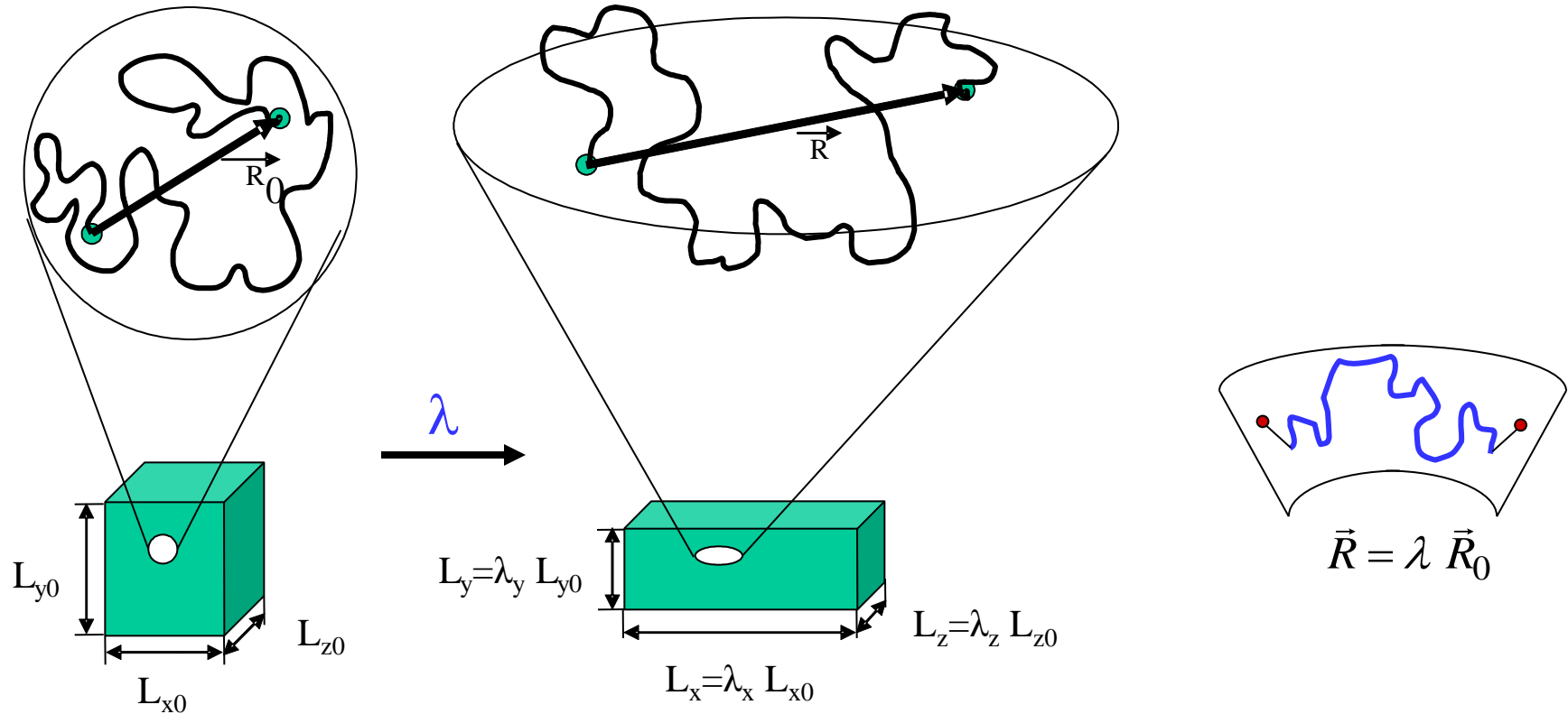
Affine network model

Deformation of the network strand is proportional
to the macroscopic deformation of the network as
if the ends of the strand are nailed to the elastic
non-fluctuating background.

Entropy of an ideal chain consisting of N Kuhn segments of length b

$$S\left(N,\vec{R}\right)=-\frac{3}{2}k\frac{\vec{R}^2}{Nb^2}+S\left(N,0\right)=-\frac{3}{2}k\frac{R_x^2+R_y^2+R_z^2}{Nb^2}+S\left(N,0\right)$$

Entropy change upon affine deformation

$$S\left(N,\vec{R}\right)-S\left(N,\vec{R}_0\right)=-\frac{3}{2}k\frac{\left(\lambda_x^2-1\right)R_{x0}^2+\left(\lambda_y^2-1\right)R_{y0}^2+\left(\lambda_z^2-1\right)R_{z0}^2}{Nb^2}$$

Entropy change for the whole network consisting of n strands

$$\Delta S_{net}=-\frac{3}{2}k\frac{\left(\lambda_x^2-1\right)\sum_{i=1}^{n}\left(R_{x0}^2\right)_i+\left(\lambda_y^2-1\right)\sum_{i=1}^{n}\left(R_{y0}^2\right)_i+\left(\lambda_z^2-1\right)\sum_{i=1}^{n}\left(R_{z0}^2\right)_i}{Nb^2}$$

In undeformed state
$$\sum_{i=1}^{n}\left(R_{x0}^2\right)_i=\sum_{i=1}^{n}\left(R_{y0}^2\right)_i=\sum_{i=1}^{n}\left(R_{z0}^2\right)_i=\frac{n}{3}Nb^2$$

Deformation free energy:
$$\Delta F_{net}=-T\Delta S_{net}=\frac{nkT}{2}\left(\lambda_x^2+\lambda_y^2+\lambda_z^2-3\right)$$

Swelling of Polymer Gels
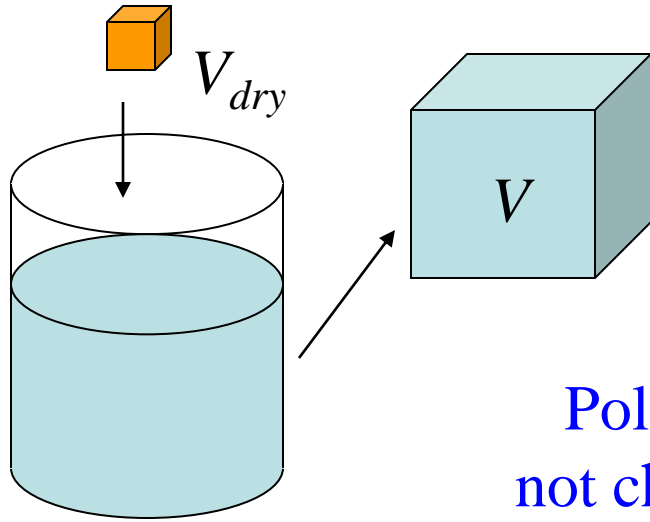
$$\phi = \frac{V_{dry}}{V}$$

volume fraction of polymer in a swollen gel

ϕ_0 − volume fraction in gel preparation state with volume V_0

Polymer amount does not change upon swelling

$$V_0\phi_0 = V\phi = V_{dry}$$

Isotropic deformation of uniformly swollen gel: $\lambda = \left| V/V_0 \right|^{1/3} = \left| \phi_0/\phi \right|^{1/3}$

Elastic free energy of a strand in a swollen gel

$$F_{el} \approx kT\frac{R^2}{R_{ref}^2} \approx kT\frac{\left(\lambda R_0 \right)^2}{R_{ref}^2}$$

(affine deformation)

Elastic free energy density

$$G\left(\phi \right) \approx \frac{kT}{b^3}\frac{\phi}{N}\frac{\left(\lambda R_0 \right)^2}{R_{ref}^2}$$

Swelling in θ-solvents

Size of a free chain in θ-solvent is independent of concentration

$$R_{ref}^2 \approx R_0^2 \approx b^2 N$$

Elastic modulus $\quad G(\phi) \approx \dfrac{kT}{b^3}\dfrac{\phi}{N}\lambda^2 \approx \dfrac{kT}{b^3}\dfrac{\phi}{N}\left(\dfrac{\phi_0}{\phi}\right)^{2/3} \approx \dfrac{kT}{Nb^3}\phi_0^{2/3}\phi^{1/3}$

Osmotic pressure in a θ-solvent: $\qquad \Pi \approx \dfrac{kT}{b^3}\phi^3$

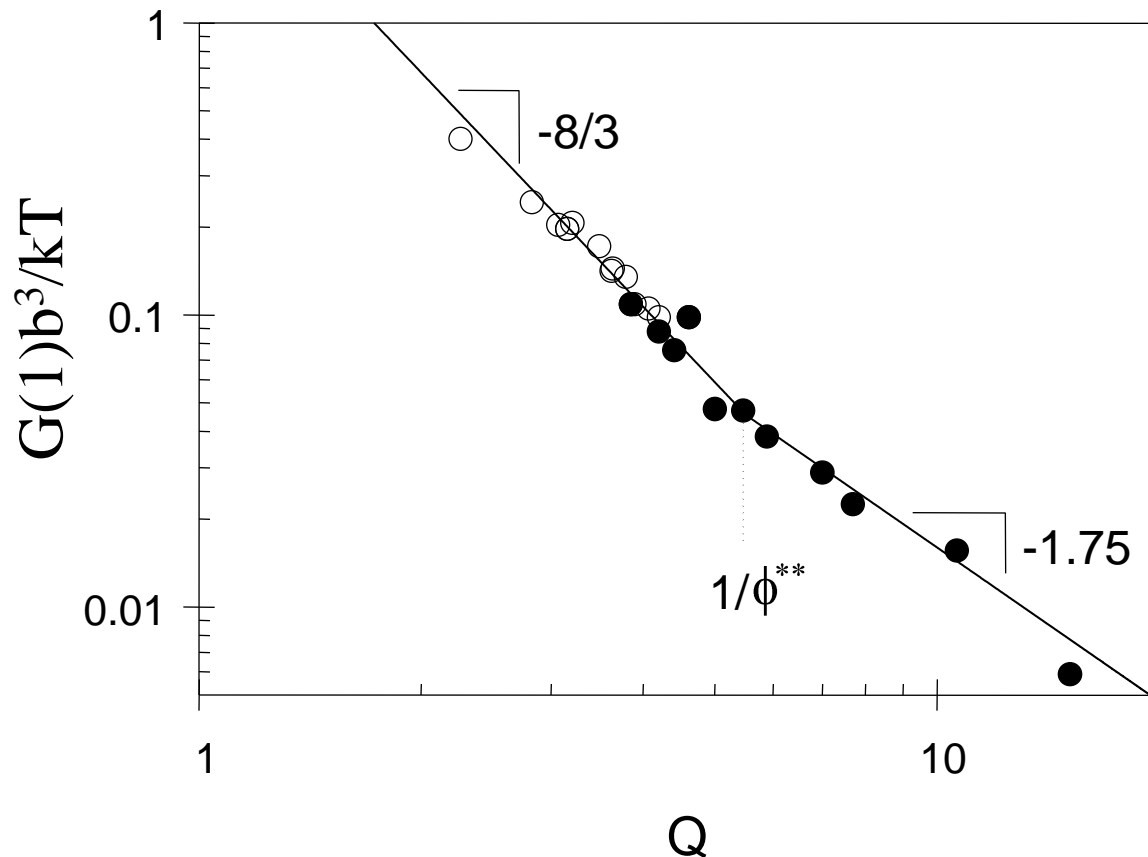Swelling equilibrium - elasticity is balanced by osmotic pressure:

$$G \approx \Pi$$

Swelling ratio: $\quad Q = \dfrac{1}{\phi} = \dfrac{V}{V_{dry}} \approx \dfrac{N^{3/8}}{\phi_0^{1/4}}$

Dry Modulus vs. Equilibrium Swelling

If network is prepared in the dry state $\phi_0 = 1$ and $N \approx Q^{8/3}$

Network modulus in the dry state $\quad G(1) \approx \dfrac{kT}{Nb^3} \phi_0^{2/3} \approx \dfrac{kT}{b^3} Q^{-8/3}$

Patel et al., *Macromolecules* **25**, 5241 (1992)

PDMS networks in toluene

Swelling in good solvents

Size of a free chain in good solvent depends on concentration

$$R_{ref} \approx R_0 \approx bN^{1/2}\phi^{-1/8}$$

Elastic modulus

$$G(\phi) \approx \frac{kT}{b^3}\frac{\phi}{N}\frac{\langle R_0 \rangle^2}{R_{ref}^2} \approx \frac{kT}{b^3}\frac{\phi}{N}\left(\frac{\phi_0}{\phi}\right)^{2/3}\left(\frac{\phi}{\phi_0}\right)^{1/4} \approx \frac{kT}{Nb^3}\phi_0^{5/12}\phi^{7/12}$$

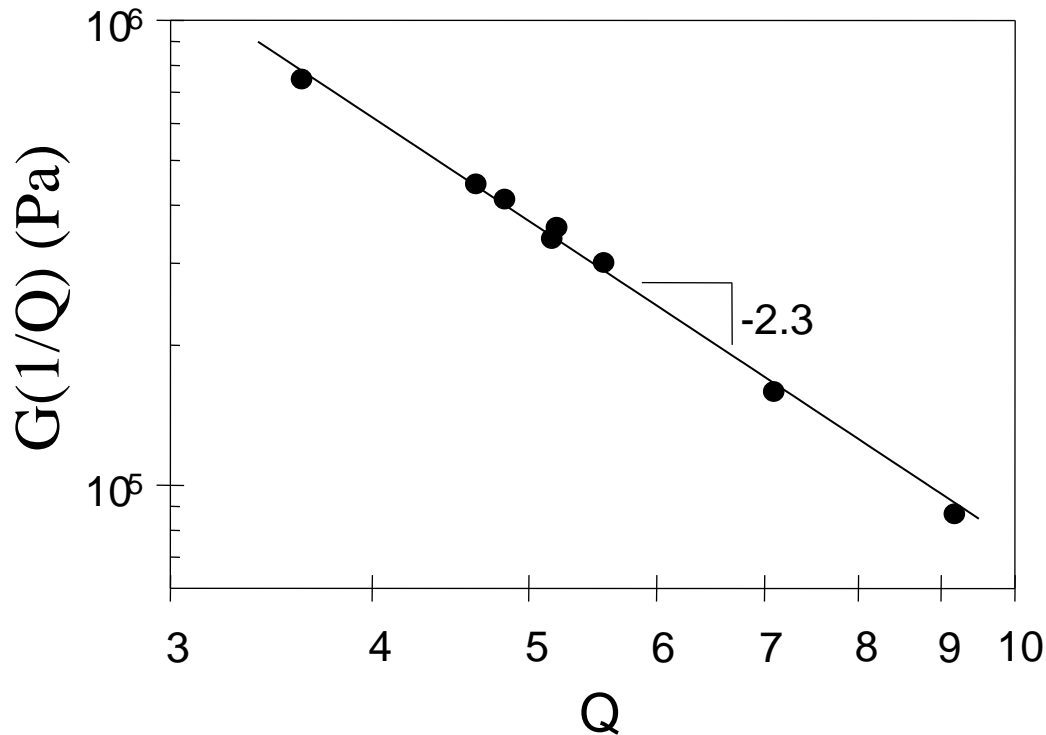Osmotic pressure in good solvent $\qquad \Pi \approx \dfrac{kT}{b^3}\phi^{9/4}$

Equilibrium swelling $\ G \approx \Pi\ $ with swelling ratio $\quad Q = \dfrac{1}{\phi} \approx \dfrac{N^{3/5}}{\phi_0^{1/4}}$

If network is prepared in the dry state: $\phi_0 = 1$ and $N \approx Q^{5/3}$

Dry Modulus vs. Equilibrium Swelling

Network modulus in the dry state $\quad G(Q) \approx \dfrac{kT}{Nb^3}\phi_0^{5/12} \approx \dfrac{kT}{b^3}Q^{-5/3}$

Network modulus at equilibrium swelling $\quad G(1/Q) \approx \dfrac{kT}{b^3}Q^{-2.3}$

End-linked PDMS networks in toluene at 25 °C.

Urayama et al., *J. Chem. Phys.* **105**, 4833 (1996).

Deformation of gels

What is the difference between gels and rubber?

1. Gels swell/deswell in response to deformation in a solvent bath. This takes time – on short time scales gels respond to deformation like rubber!

2. Swelling effects on entanglements (melts vs semi-dilute solutions)
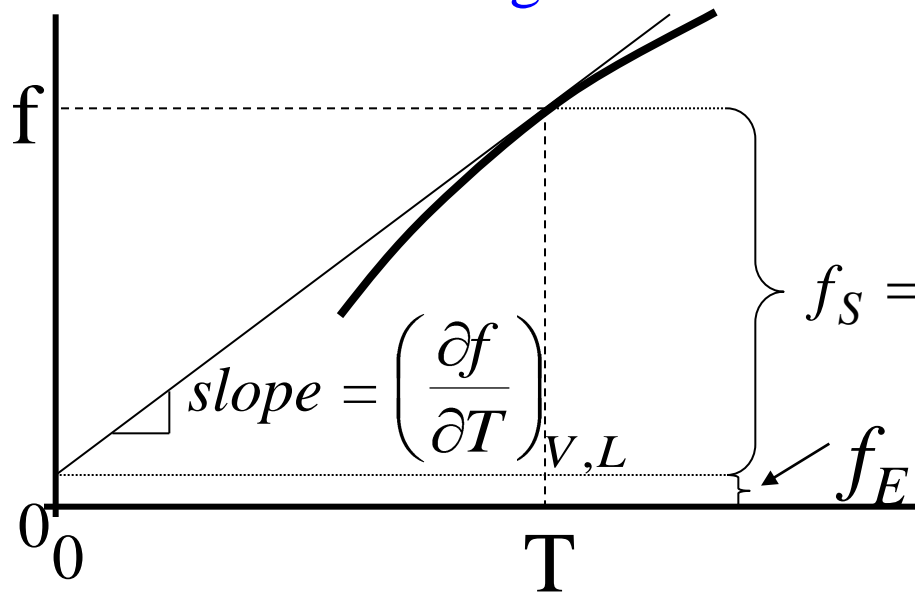
Thermodynamics of Rubber

Helmholtz free energy $\quad dF = d(U - TS) = -SdT - pdV + fdL$

Applied force $\quad f = \left(\dfrac{\partial F}{\partial L}\right)_{T,V} = \left[\dfrac{\partial (U - TS)}{\partial L}\right]_{T,V} = \left(\dfrac{\partial U}{\partial L}\right)_{T,V} - T\left(\dfrac{\partial S}{\partial L}\right)_{T,V}$

is the sum of two contributions $\quad f = f_E + f_S$

Maxwell relation $\quad \left(\dfrac{\partial S}{\partial L}\right)_{T,V} = -\left(\dfrac{\partial f}{\partial T}\right)_{V,L}$

Force at constant elongation

$slope = \left(\dfrac{\partial f}{\partial T}\right)_{V,L}$

Entropic contribution dominates

$f_S = T\left(\dfrac{\partial f}{\partial T}\right)_{V,L} = -T\left(\dfrac{\partial S}{\partial L}\right)_{T,V}$

Energetic contribution

$f_E = \left(\dfrac{\partial U}{\partial L}\right)_{T,V}$

Uniaxial deformation of incompressible networks

$$V_0 = V; \quad L_{x0}L_{y0}L_{z0} = L_x L_y L_z = \lambda_x L_{x0} \lambda_y L_{y0} \lambda_z L_{z0}$$

$$\lambda_x \lambda_y \lambda_z = 1$$

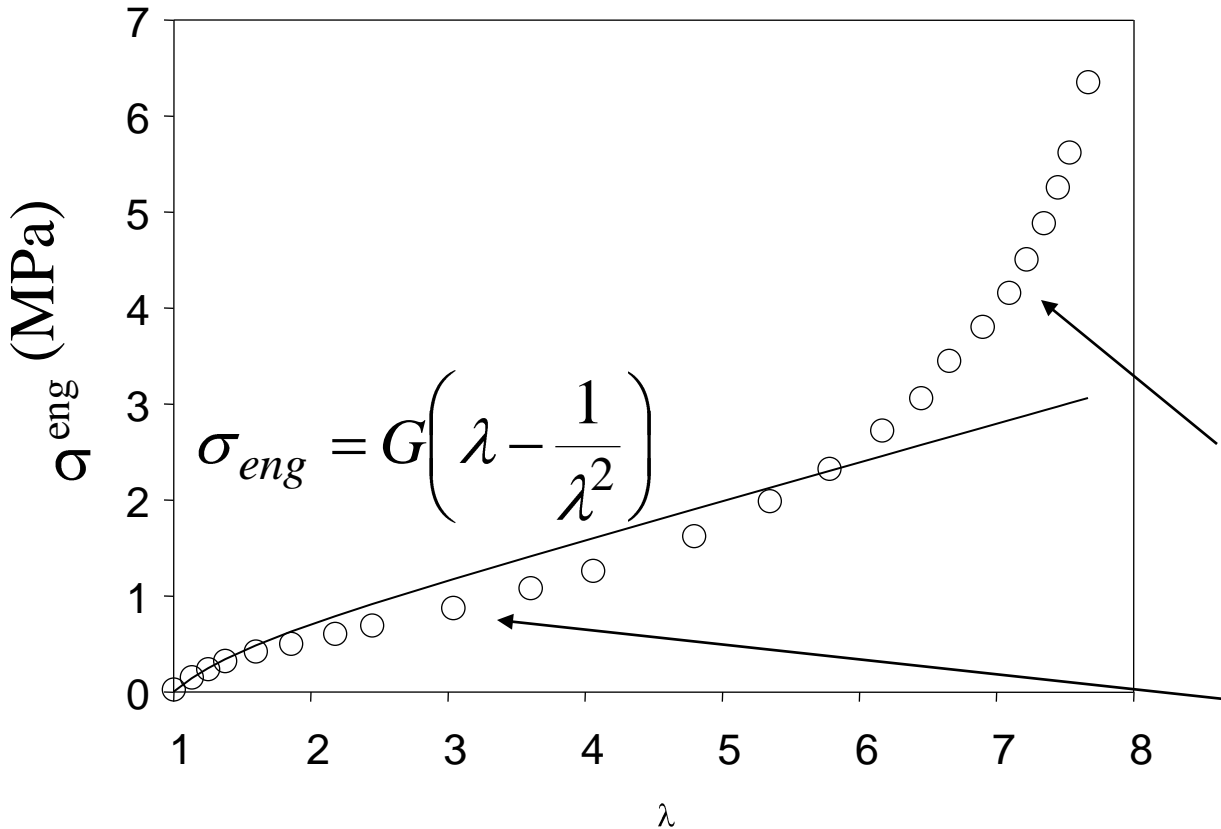Uniaxial deformation $\lambda_x = \lambda \qquad \lambda_y = \lambda_z = \lambda^{-1/2}$

Free energy change: $\quad \Delta F_{net} = \dfrac{nkT}{2}\left(\lambda^2 + \dfrac{2}{\lambda} - 3 \right)$

Force $\qquad f_x = \dfrac{\partial \Delta F_{net}}{\partial L_x} = \dfrac{\partial \Delta F_{net}}{\partial \lambda L_{x0}} = \dfrac{1}{L_{x0}} \dfrac{\partial \Delta F_{net}}{\partial \lambda} = \dfrac{nkT}{L_{x0}}\left(\lambda - \dfrac{1}{\lambda^2} \right)$

Stress $\qquad \sigma_{xx} = \dfrac{f_x}{L_y L_z} = \dfrac{nkT}{L_{x0}L_{y0}L_{z0}} \lambda\left(\lambda - \dfrac{1}{\lambda^2} \right) = \dfrac{nkT}{V}\left(\lambda^2 - \dfrac{1}{\lambda} \right)$

Modulus (affine) $\qquad G = \dfrac{nkT}{V} = \dfrac{ckT}{N}$

Deviations from Classical Stress-Strain Dependence

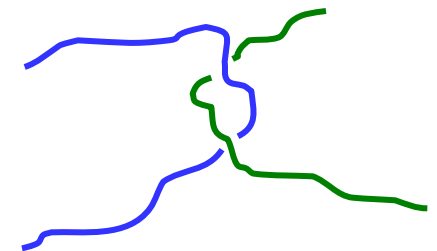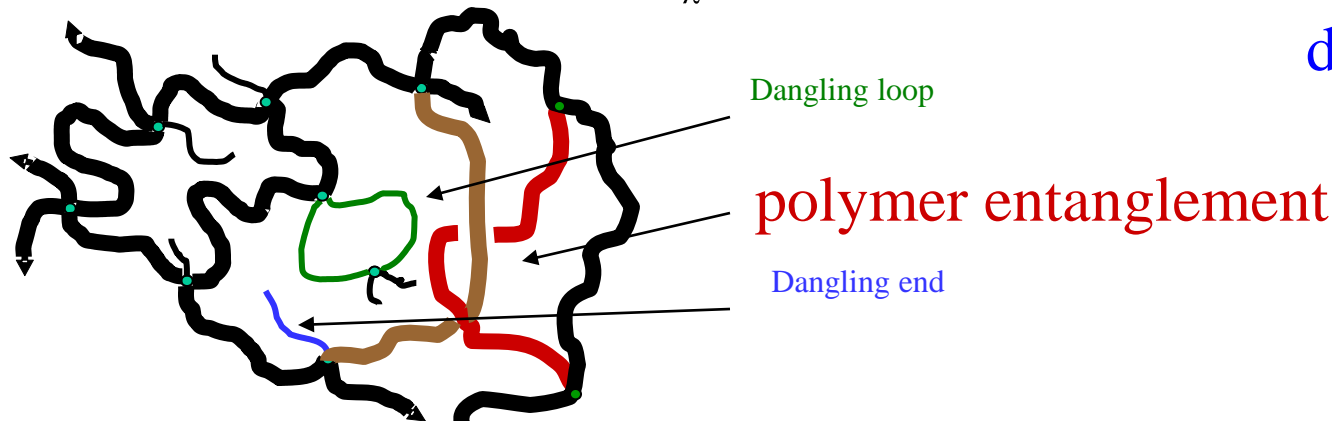$$\sigma_{eng} = G\left(\lambda - \frac{1}{\lambda^2}\right)$$
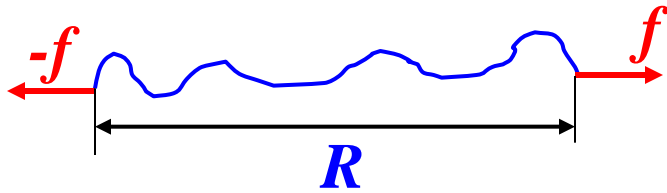
Engineering stress

$$\sigma_{eng} = \frac{f_x}{L_{y0}L_{z0}} = \frac{\sigma_{true}}{\lambda}$$

Strain hardening at large elongations due to finite chain extensibility.

Strain softening at small elongations due to entanglements.

Dangling loop

polymer entanglement

Dangling end

Strain Hardening at Large Elongations

-f   f

R

Gaussian   Freely jointed   Worm-like

$\langle R \rangle / R_{max}$ $fb/(kT)$

Gaussian chain: linear force – elongation dependence $\vec{f} = \dfrac{3kT}{Nb^2} \vec{R}$

Real polymers cannot be extended beyond maximum contour length R_{max}

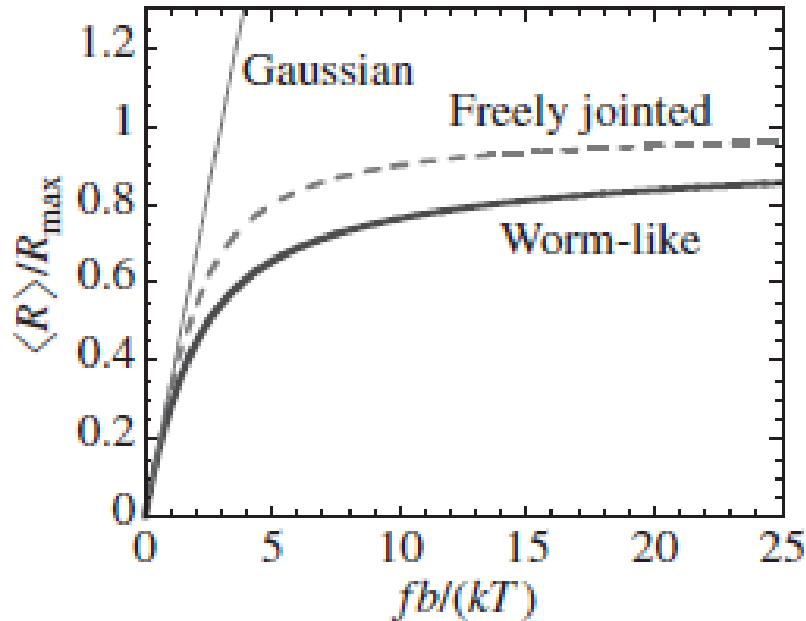Force f diverges as $R \rightarrow R_{max}$

Divergence rate depends on chain flexibility:

Flexible chains are described by freely-jointed chain model with

$$f \sim (R_{max} - R)^{-1}$$

Semi-flexible chains are described by worm-like chain model with $\quad f \sim (R_{max} - R)^{-2}$
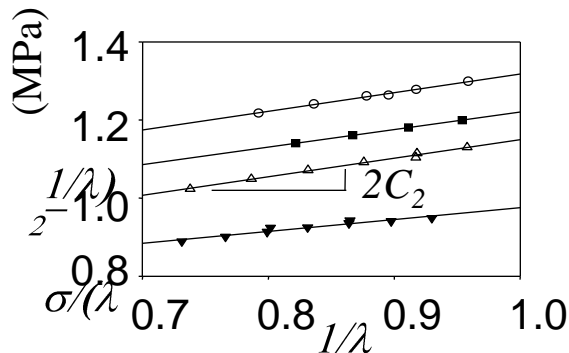
Mooney – Rivlin model of incompressible networks:

Strain invariants: $I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2$ $\qquad$ $I_2 = \lambda_x^2\lambda_y^2 + \lambda_y^2\lambda_z^2 + \lambda_z^2\lambda_x^2$

Free energy density:

$$\frac{F}{V} = C_1(I_1 - 3) + C_2(I_2 - 3) = C_1\left(\lambda^2 + \frac{2}{\lambda} - 3\right) + C_2\left(2\lambda + \frac{2}{\lambda^2} - 3\right)$$

Stress

$$\sigma_{true} = \frac{1}{L_y L_z}\frac{\partial \lfloor F/V \rfloor}{\partial \lambda} = \lambda\frac{\partial \lfloor F/V \rfloor}{\partial \lambda} = 2C_1\left(\lambda^2 - \frac{1}{\lambda}\right) + 2C_2\left(\lambda - \frac{1}{\lambda^2}\right)$$
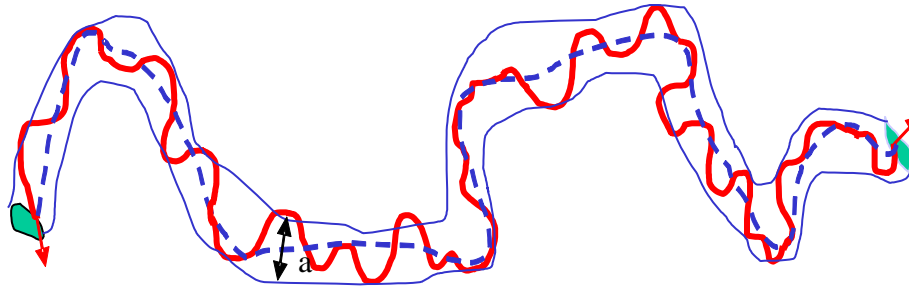
Mooney-Rivlin equation

$$\frac{\sigma_{true}}{\lambda^2 - 1/\lambda} = 2C_1 + \frac{2C_2}{\lambda}$$

Deviations from classical elasticity at intermediate deformations: Entanglements?

Edwards Tube Model

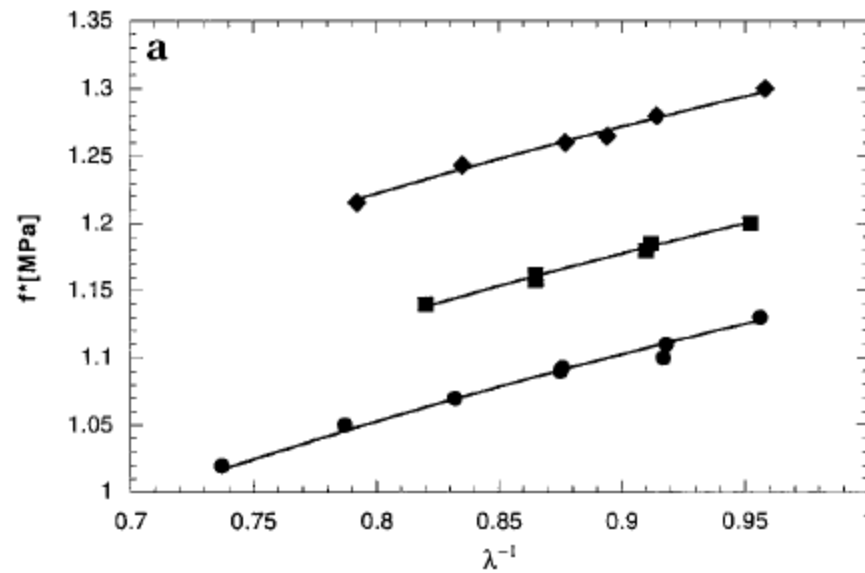N_x – degree of polymerization between crosslinks

$N_e \sim (a/b)^2$ – degree of polymerization between entanglements

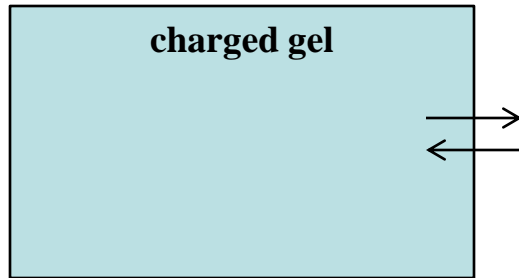Affine modulus $\qquad G = kT\, \dfrac{c}{N_x} + kT\, \dfrac{c}{N_e}$

Non-Affine Tube Model

Confining potential and tube diameter change with network deformation

Mooney stress: $\quad f^* = \dfrac{\sigma}{\lambda^2 - 1/\lambda} = G_x + G_e \dfrac{1}{\lambda - \lambda^{1/2} + 1}$

Rubinstein & Panyukov, Macromolecules **1997,** 30, 8036

Swelling Equilibrium in Charged Gels:

charged gel   **solvent**

Donnan equilibrium
for salt ions (c_s) and counterions (fc)

f- degree of ionization;   c- monomer concentration

Π_{el} - electrostatic contribution to osmotic pressure

For fc » $2c_s$ - ideal gas of counterions: Π_{el}

For fc « $2c_s$, : Π_{el} $\underline{(\quad)}$

Osmotic modulus: $\Pi = \Pi_0 + \Pi_{el}$

$\uparrow$

osmotic pressure in a in semi-dilute solution (c^2 in ideal
and $c^{2.25}$ in good solvent)

Exact solution:

Concentration of salt ions outside the gel: c_s

Concentration of ions inside the gel: c_+ and c_-

Equating inside and outside chemical potentials for each type of ions:

$$c_+ = \qquad c_s \qquad\qquad\qquad c_- = \qquad c_s$$

Electroneutrality (negatively charged gel):

$$3.\ e(-fc + c_+ - c_-) = 0$$

Solution: $c_{+/-} = -\left(\qquad \sqrt{(\quad)} \quad \right)$

$\Pi_{el} \qquad\qquad + \quad (\quad) \qquad \sqrt{(\quad)}$
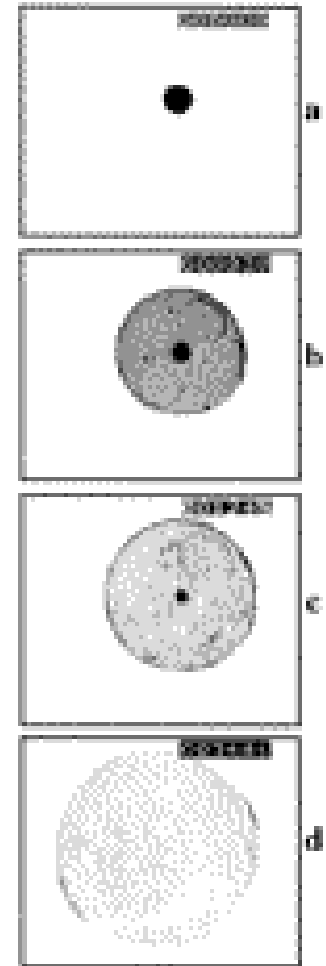
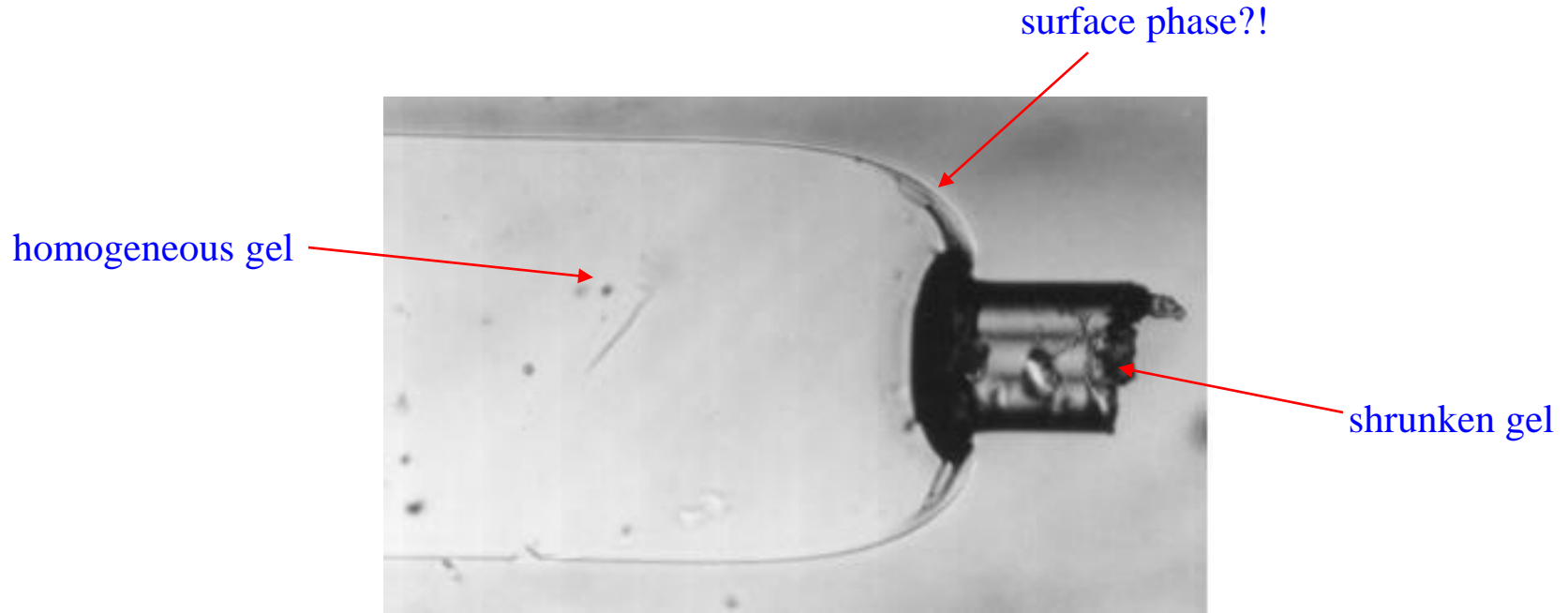Elastic modulus for isotropic swelling (ideal chains, no electrostatic effects on conformation):

$$G= \text{—} \lambda^2 = \text{—} \left(-\right)$$

Swelling equilibrium: $\Pi = G$

poly(0.75 sodium acrylate−0.25 acrylic acid) gel in water

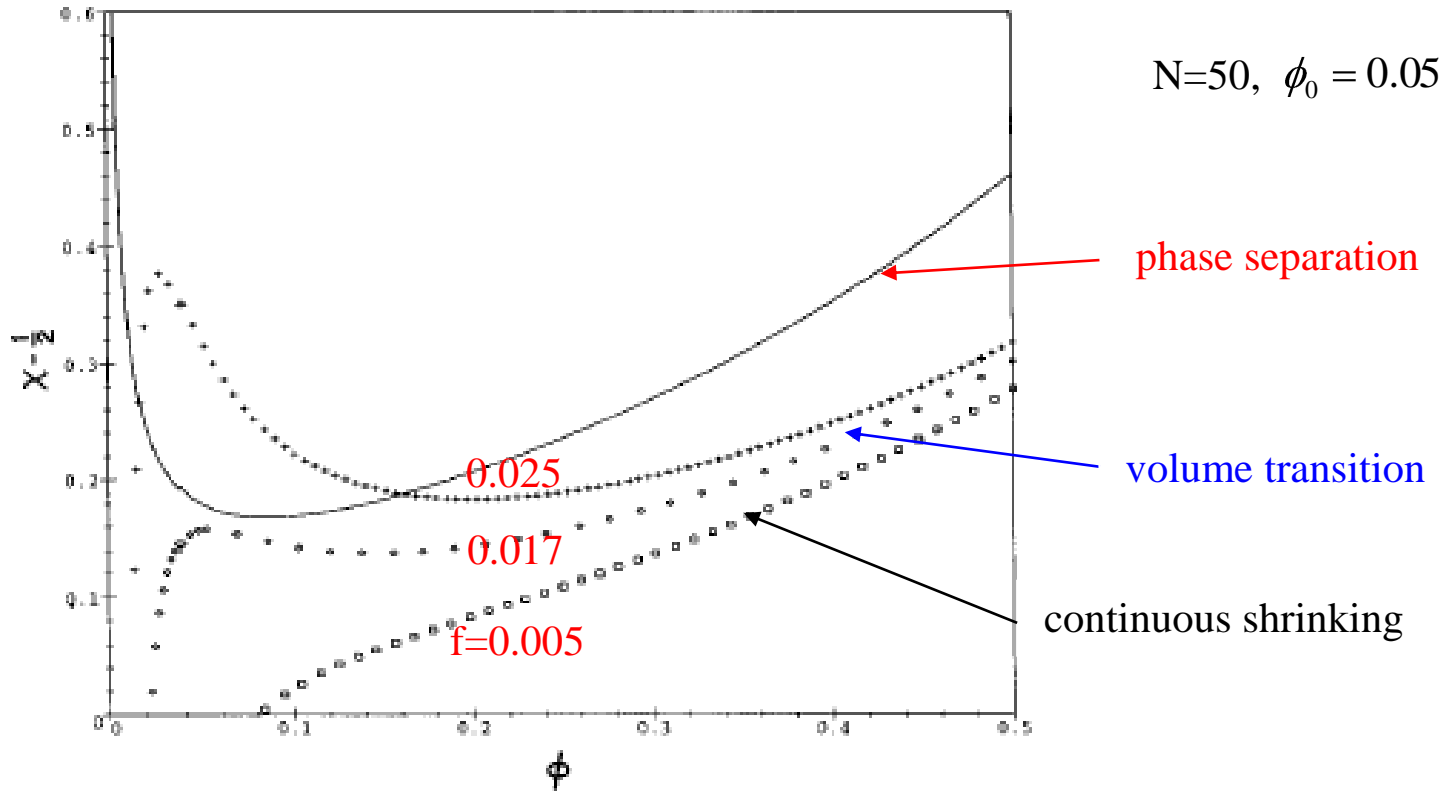# Volume Transition and Phase Separation in Charged Gels
(change T)

NIPA/AAc (668mM/12mM) gel in water
at 35 ºC

Courtesy M. Shibayama

Salt-free case:

Free energy
(per monomer)

$$\frac{\mathcal{F}_0\{\lambda_\alpha\}}{T} = \frac{1}{4N}\sum_\alpha \lambda_\alpha^2 - \chi\phi + \frac{1-\phi}{\phi}\ln(1-\phi) + f\ln\phi$$

N=50, $\phi_0 = 0.05$

phase separation

volume transition
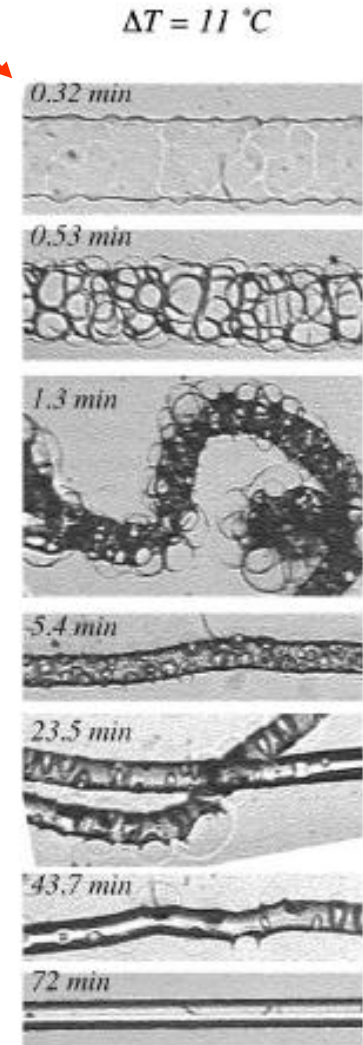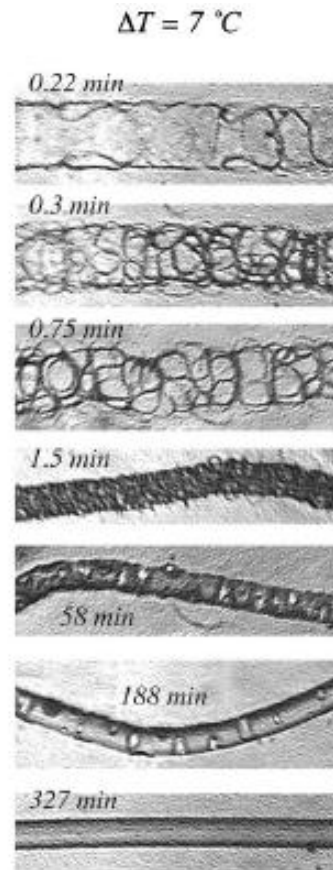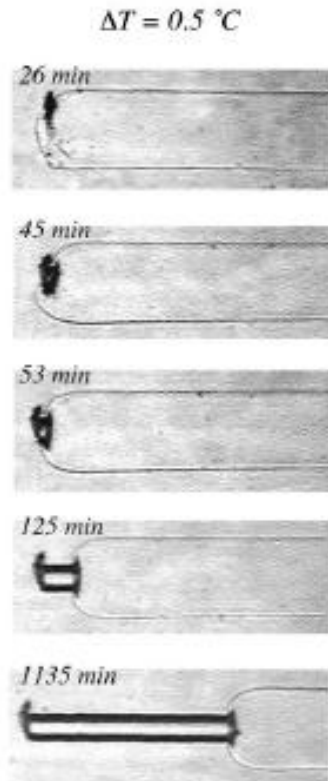
continuous shrinking

0.025

0.017

f=0.005

f– degree of ionization

Phase transitions in NIPA-AA gels

Volume transition
(shallow quench)

Initial microphase separation
followed by volume transition
(deep quench)

$\Delta T = 0.5\ °C$

$\Delta T = 7\ °C$

$\Delta T = 11\ °C$

0.15mm

26 min

45 min

53 min

125 min

1135 min

0.22 min

0.3 min

0.75 min

1.5 min

58 min

188 min

327 min

0.32 min

0.53 min

1.3 min

5.4 min

23.5 min

43.7 min

72 min

What about the microscopic structure of gels on length scales < 1 micron?

Scattering experiments from mesoscales (LS)
to nanoscales (SANS, SAXS):

Frozen inhomogeneities, topological disorder, thermal fluctuations

Monomer concentration inhomogeneities (and therefore scattering from gels) diverge at ϕ_C^*. Since ordinary "solid" gels are formed considerably above the gel point, one expects inhomogeneities to decrease with increasing crosslink concentration.
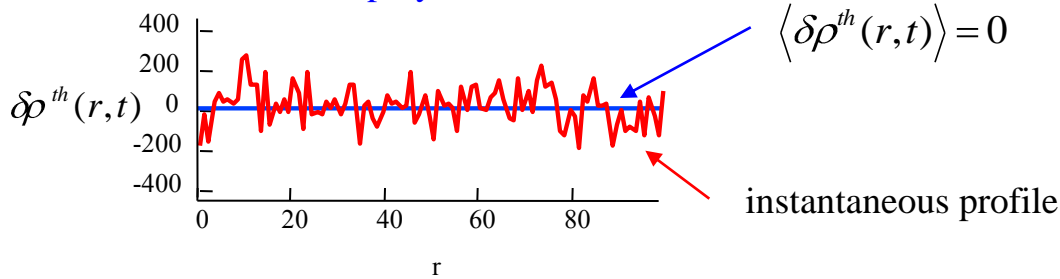
Experiment:

S. Mallam et al., *Macromolecules*, **1989**, 22, 3356
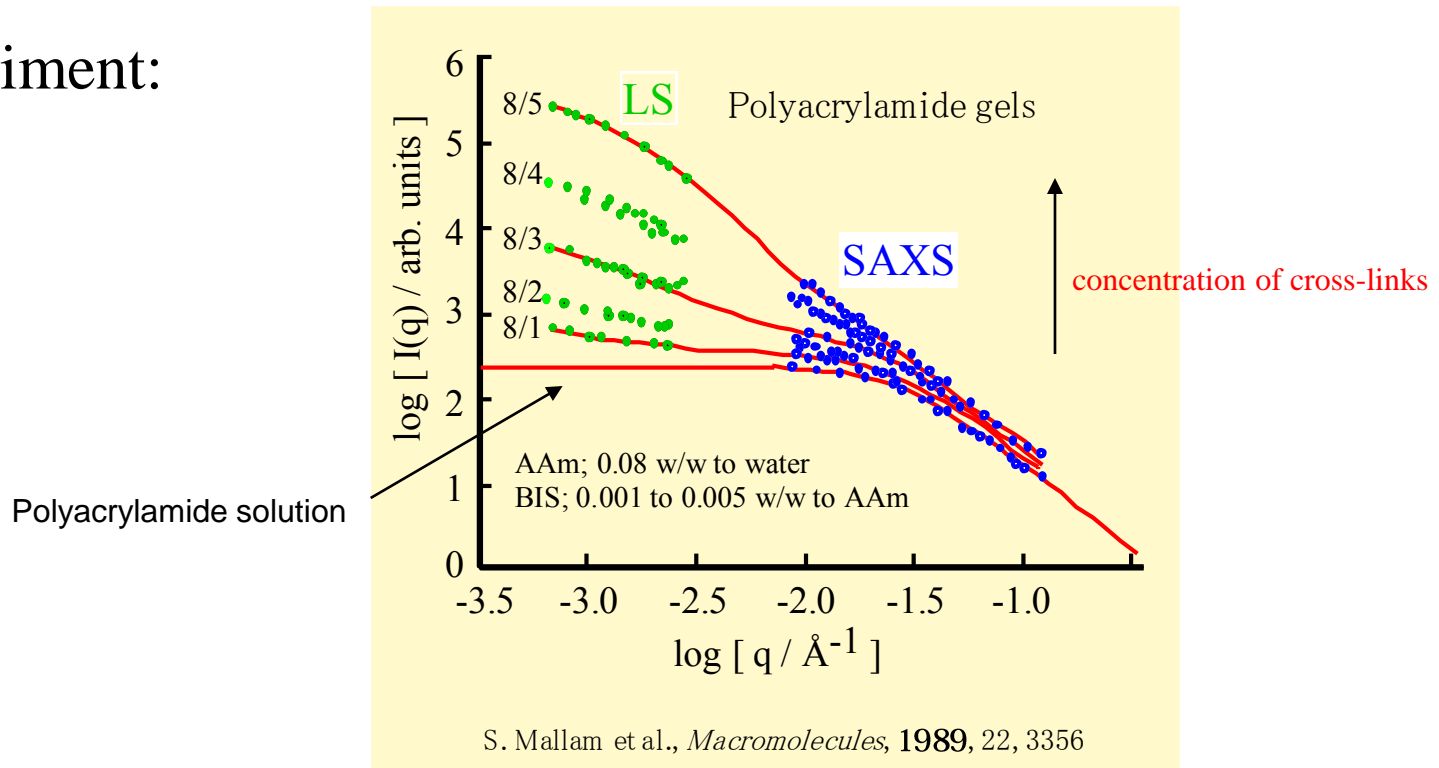
$$\langle \rho(r,t)\rangle = \rho^{eq}(r) \quad \text{thermal (time) average} \qquad \overline{\rho(r)} \quad \text{spatial (ensemble) average}$$

$$\delta\rho^{th}(r,t) = \rho(r,t) - \rho^{eq}(r)$$

Thermal fluctuations in polymer solutions

$$\langle \delta\rho^{th}(r,t)\rangle = 0$$

instantaneous profile

$$S(\mathbf{q}) \equiv \langle \rho(\mathbf{q})\rho(-\mathbf{q})\rangle = \langle \rho^{th}(\mathbf{q})\rho^{th}(-\mathbf{q})\rangle \equiv G(\mathbf{q})$$
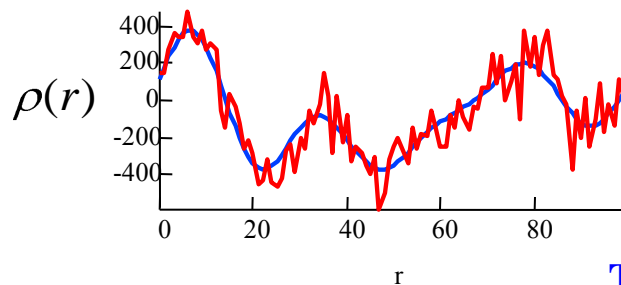
Thermal correlator

Static inhomogeneities in gels
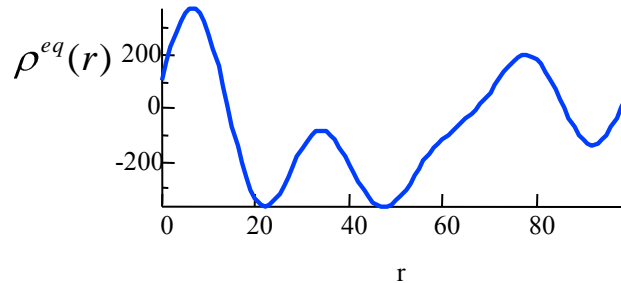
$$C(\mathbf{q}) \equiv \overline{\rho^{eq}(\mathbf{q})\rho^{eq}(-\mathbf{q})} \qquad \text{Static correlator}$$
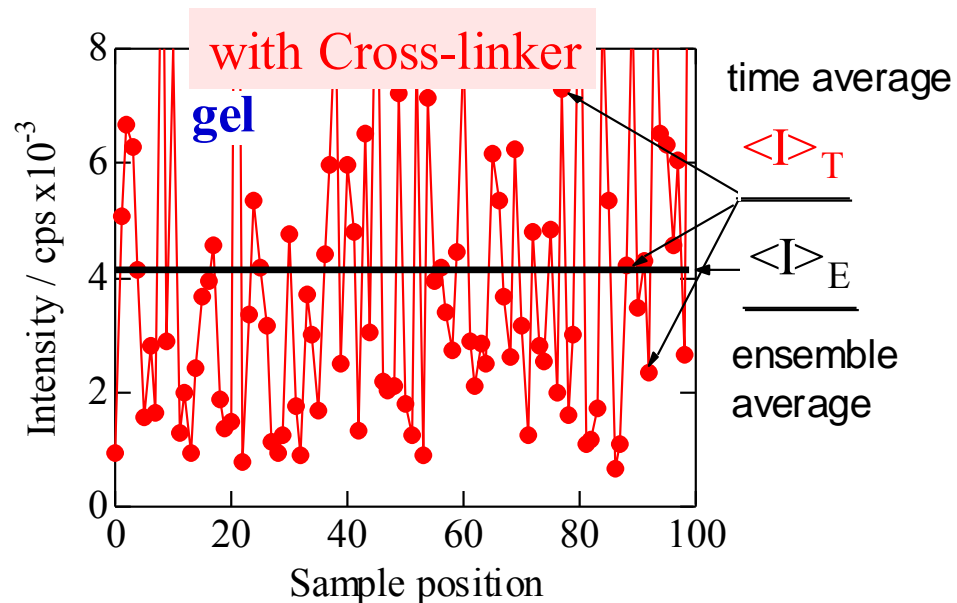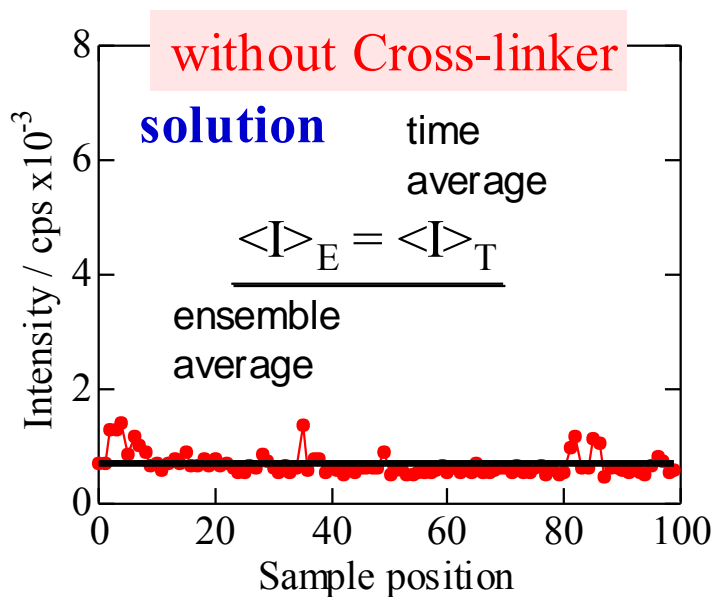
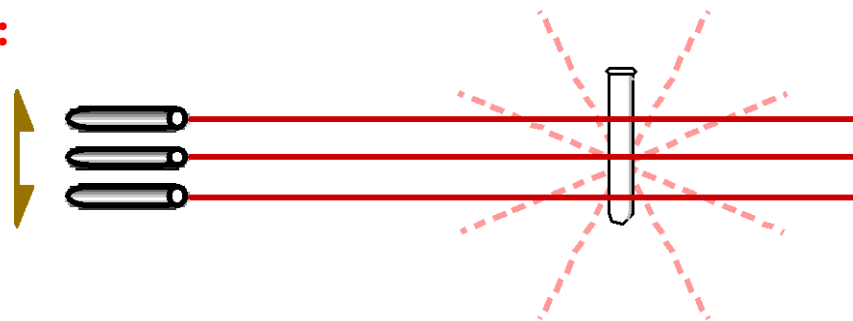**Static inhomogeneities and thermal fluctuations in gels**

$$S(\mathbf{q}) \equiv \overline{\langle \rho(\mathbf{q})\rho(-\mathbf{q})\rangle} = C(\mathbf{q}) + G(\mathbf{q})$$

The total structure factor is measured by scattering experiments!

Direct evidence for static inhomogeneities: stationary speckle patterns

without Cross-linker

solution

time average

$$\langle I \rangle_E = \langle I \rangle_T$$

ensemble average

with Cross-linker

gel

time average

$\langle I \rangle_T$

$\langle I \rangle_E$
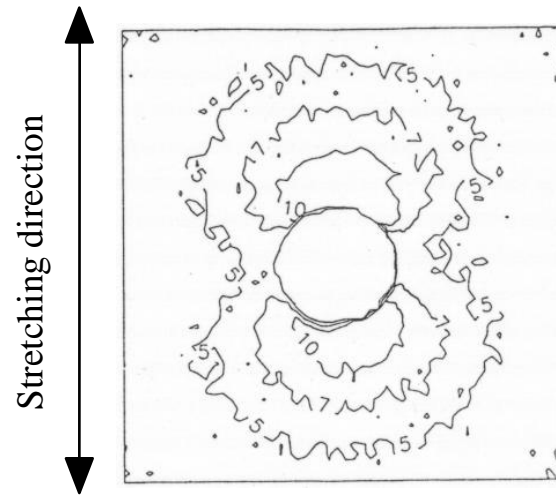
ensemble average

Pusey et al, 1991

Ergodicity broken!

The butterfly effect: scattering from stretched gels

Theory of elasticity + statistical mechanics:

Thermal fluctuations suppressed along stretching direction and enhanced normal to it

SANS experiments observe the reverse!

λ=1.58

Bastide et al, *Macromolecules* **23**, 1821 (1990)

These are not thermal fluctuations!

Stretching enhances density contrast between heavily and lightly crosslinked regions

Scattering profiles : from replica field theory calculation

("fluctuations" around the mean-field solution of the Deam-Edwards model)

Structure factor $\qquad S(\mathbf{q}) = G(\mathbf{q}) + C(\mathbf{q})$

Thermal correlator $\qquad G = G(Q, \varphi, \chi)$

$$\left| Na^2/6 \right|^{1/2} q$$

reduced scattering vector $\qquad$ concentration $\quad$ interaction parameter

Static correlator $\qquad C = C(Q, \varphi, \chi; \varphi_0, \chi_0)$

parameters at state of preparation

A gel "remembers" not only its topology but also the concentration and temperature at which it was prepared!

Panyukov and Rabin,
Phys. Rep. **269**, 1 (1996)
Macromolecules **29**, 7960 (1996).

For gels prepared by reacting monomers -crosslinks act as attractions

Increasing concentration of crosslinks and/or decreasing solubility during gelation − approach spinodal of the monomer-crosslink system

P.-G. de Gennes, Scaling Methods in Polymer Physics (1979)
S.V. Panyukov and Y. Rabin, *Phys. Rep.* **269**, 1 (1996)
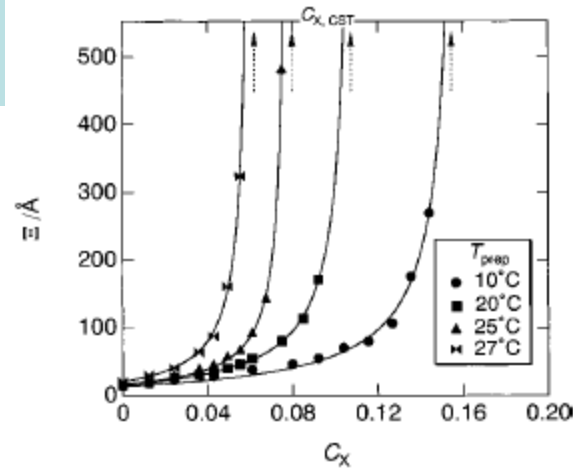
Crosslink saturation threshold

$$C(q = 0) \rightarrow \infty \quad \text{at the CST}$$

Length scale of static inhomogeneities : $\rightarrow$
(effective mesh size)
$$\begin{cases} aN^{1/2} & \text{away from CST} \\ \\ \infty & \text{at CST} \end{cases}$$

No CST for gels prepared by irradiation crosslinking

Test of CST

Correlation length of static inhomogeneities
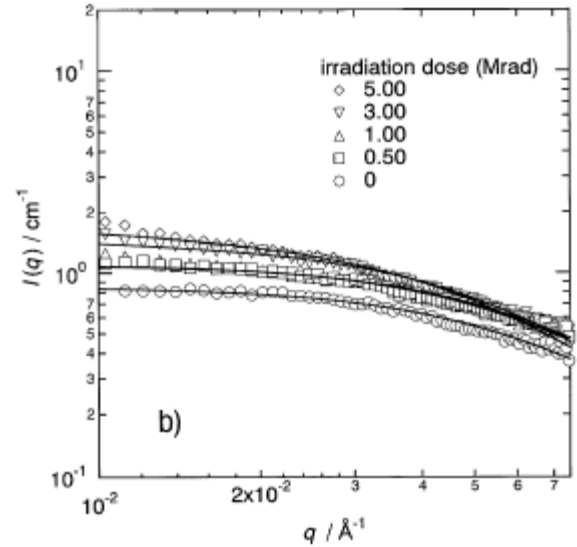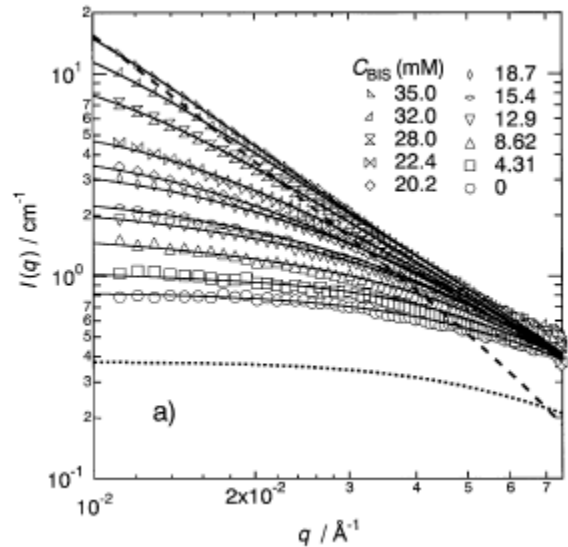
Crosslink concentrration

Noritsue et al, *Polymer* **43**, 5289 (2002)

Inhomogeneities are revealed upon swelling since highly crosslinked regions swell less than those that are poorly crosslinked.

Fitting scattering profiles with PR theory:

Reacting monomer- crosslink mixture
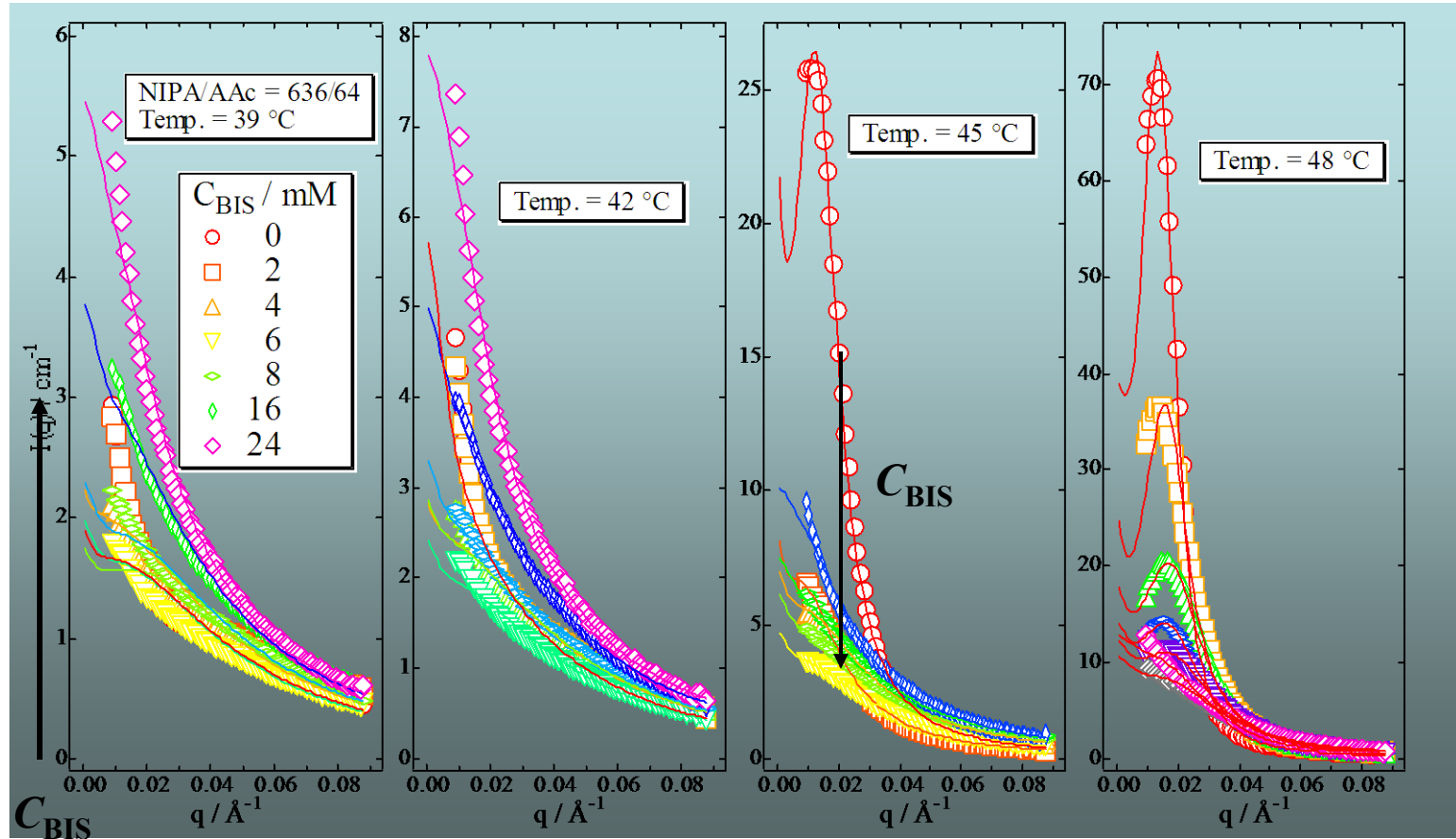
Irradiation crosslinking of chains

a)

b)
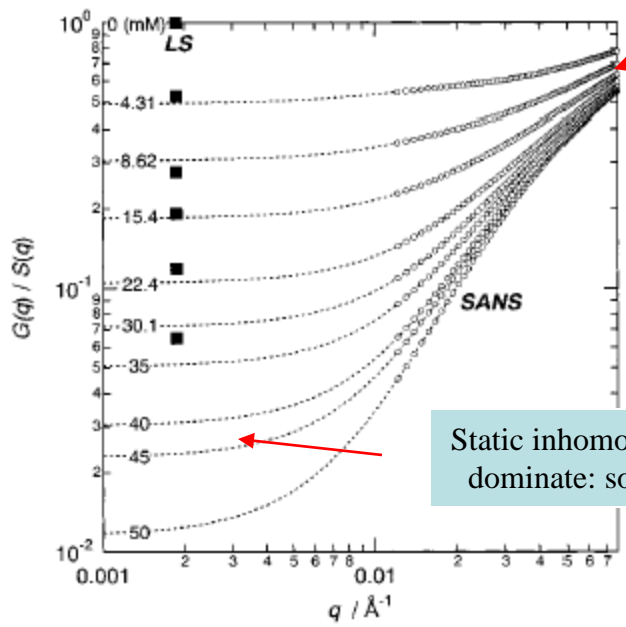
Strong thermal fluctuations:
liquid-like

Static inhomogeneities
dominate: solid-like

Noritsue et al, *Polymer* **43**, 5289 (2002)
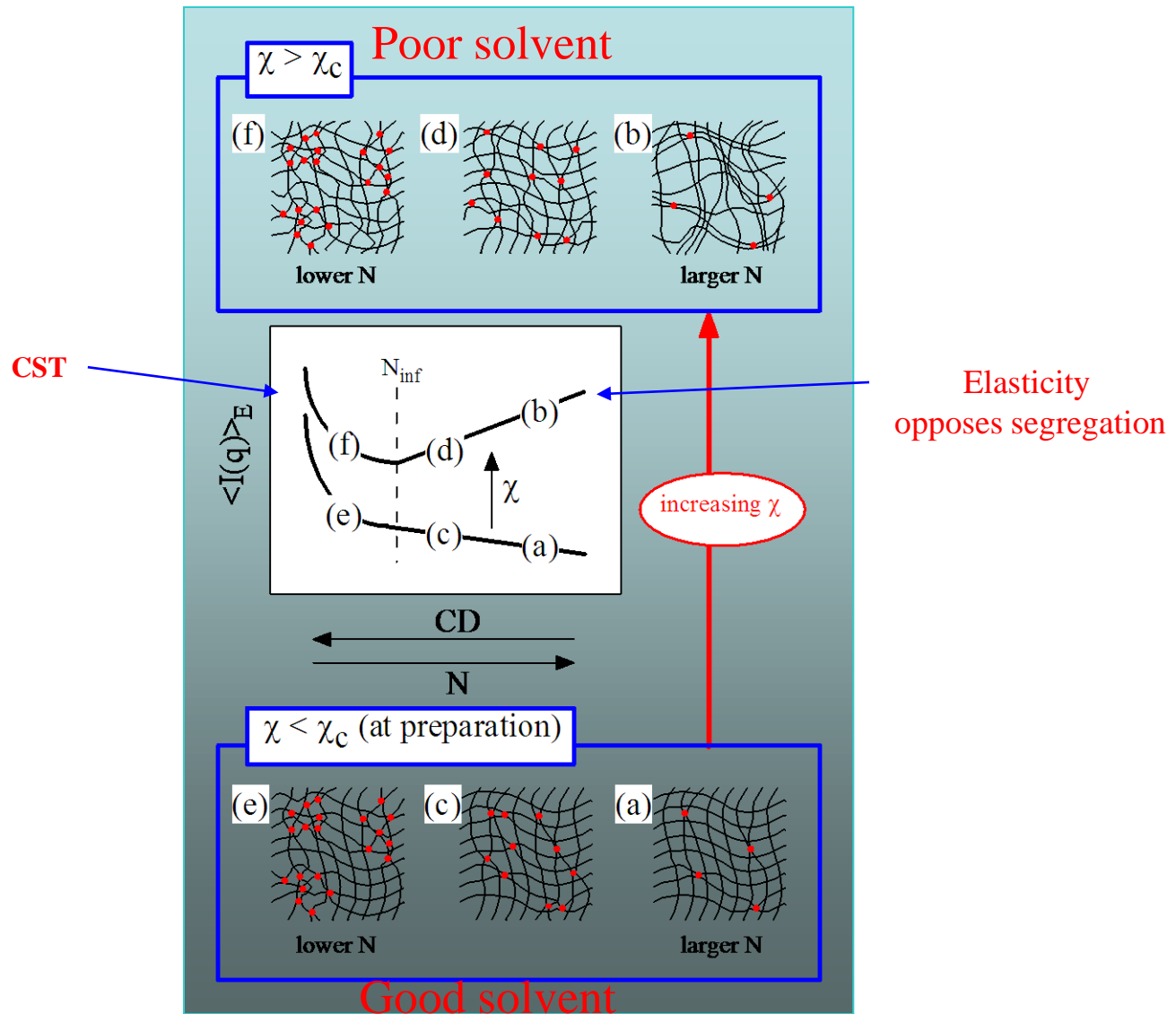Takata et al, *Macromolecules* **35**, 4779 (2002)

Temperature and cross-link density dependence: SANS vs. theory

Peak at q* comes from static inhomogeneities, not thermal fluctuations !

Structural reorganization subject to crosslink constraints

Ikkai et al., *Macromolecules* **31**, 151 (1998)

Crosslink concentration dependence

Ikkai and Shibayama, *Phys. Rev. E* Rapid Commun., 1997; Panyukov and Rabin, *Physica A* **249**, 239 (1998)

SANS from deformed NIPA/AAc gel

Static inhomogeneities dominate away from T_{MST}

Thermal fluctuations dominate near T_{MST}

Shibayama et al, *Macromolecules* **31**, 2586, (1998)